

A NEW CHEMICAL METHOD FOR PURIFICATION AND SURFACE MODIFICATION OF SRI LANKAN VEIN GRAPHITE

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ABSTRACT: Sri Lanka has its own demarcated possession for the high quality vein graphite containing 95-98 % of initial purity of carbon. Presently Sri Lankan vein graphite is exported as a cheap raw material without any value addition. The present study focuses to find a cost effective and convenient new chemical method for the graphite purification and to modify the graphite surface using alkali chloride solutions for improving performance of a graphite electrode (for negative electrode) of batteries. Collected vein graphite samples were powdered and prepared samples (10 g of <math>< 53 \mu\text{m}</math>) were treated for acid digestion method with a mixture of 5 % of HF, Con.H₂SO₄ & Con.HNO₃. 3.50 g of portions graphite powders were separately mixed with 100 ml of 0.1% LiCl, 0.1% KCl and 0.1 % NaCl aqueous solutions for preparing of surface modified graphite. The carbon content of the Needle Platy Graphite (NPG) variety has the highest carbon content and the purity of the samples has been enhanced after acid digestion treatment by removing impurities. The FTIR analysis proved that many of impurity related functional group bands have been removed from the surface modified NPG. The Lithium, Sodium and Potassium Chloride coatings were capable to improve the electric conductivity performance.

Keywords: Vein Graphite, Acid Digestion, Surface Modification

INTRODUCTION

Graphite is a commercially very important crystalline form of carbon. Sri Lanka has its own demarcated possession for the high quality vein graphite containing 95-98 % of initial purity of carbon. Sri Lankan vein graphite have been categorized into four morphologies; namely, Shiny slippery fibrous graphite (SSF), Needle platy graphite (NPG), Coarse striated flaky graphite (CSF) and Coarse flakes of radial graphite (CFR) [1]. Since the Kahatagaha-Kolongaha and the Bogala graphite mines are the two major mines in Sri Lanka, many of research studies have been focused on origin, geological structure, modifications and high tech applications [2-7].

Various thermal (Physical) and chemical purification methods have been investigated to remove the mechanically attached and intercalated impurities in natural graphite. Thermal treatments include the heating of natural graphite up to 1500 °C to 2400 °C in an inert environment, which is extremely costly [8]. Both ball milling and chemical oxidation approaches have been attempted to modify the surface properties of natural graphite. The graphite surface can be modified by chemical oxidation while the morphology and the texture of graphite can be modified by mechanical ball milling. It has been reported that these types of mechanical and chemical treatments have improved the electrochemical properties of graphite [7]. The other purifying method is the chemical treatment where graphite is reacted with mineral acids such as nitric, sulfuric, hydrochloric and hydrofluoric. However, use of strong acids is not a cost effective method [7-10].

Alkali Roasting is one of the effective chemical method that able to remove sulfide and silicate impurities from graphite [11]. An attractive way of getting some insight into the correlation between the electrochemical performance and morphology of natural graphite is to find an effective treatment method, which can significantly change some aspects of natural graphite's morphology and then alter the corresponding electrochemical performance [8].

Presently Sri Lankan vein graphite is exported as a cheap raw material without any value addition and small vein graphite mines has a less attention. Moreover, the high purity is essential to employ natural vein graphite in advance technological applications. The objective of the present study is to find a cost effective and convenient new chemical method for the graphite purification and to modify the graphite surface using alkali chloride solutions for improving performance of graphite anodes in Li-ion rechargeable batteries.

METHODOLOGY

Collected vein graphite samples were powdered and prepared samples (10 g of <math><53\ \mu\text{m}</math>) were treated with a mixture of 5 % of HF (VWR, 40 %), Con.H₂SO₄ (98 %, VWR) & Con.HNO₃ (Sigma, > 69 %) according to the acid digestion method [15]. Above prepared mixture was kept in fume hood and heated. The residue was filtered and washed with copious amount of water until the solution p^H became neutral (p^H 7). This process was carried out by vigorous stirring and vacuum filtering. Resulting wet graphite powder was dried in Oven at 100°C [9].

3.50 g of both raw and purified NPG graphite powder was measured and added into 100 ml of 0.1 % LiCl aqueous solution separately. The mixtures were stirred for 30 minutes, in order to ensure the homogeneous wetted powder. Then, graphite powders were filtered out using reduced pressure without water rinsed, and vacuum dried at 120°C. Same procedure was repeated for other raw and purified samples with 0.1 % NaCl (DAEJUNG, 99 %, 50 g l⁻¹) and 0.5 % KCl aqueous solutions.

Carbon content of raw and purified samples were analyzed by ASTM - 561 method. Selected samples were characterized with X-Ray Diffraction (XRD) by "Rigaku-Ultima IV" X-ray diffractometer, using Cu-K α 1 radiation ($\lambda = 1.54\ \text{\AA}$) and Nicolet 6700 Fourier Transform Infrared (FTIR) Spectrophotometer in 500-4000 cm⁻¹ region. Microscopic imaging of selected samples were conducted by Scanning Electron Microscope (SEM) with Energy dispersive X-ray (EDX) spectroscopy (EEVO/LS 15 ZEISS). Conductivity measurements were taken by Four-Probe DC conductivity method under different temperature conditions. Electrical conductivity calculations were carried out according to Ohm's law. Electric conductivity vs Temperature was plotted according to Arrhenius equation [12].

RESULTS AND DISCUSSION

Purity enhancement with Acid Digestion Method

Carbon contents of both raw and purified different morphologies of vein graphite are given in table 01. The carbon content varies with the crystal morphology and it is shown that NPG variety has the highest carbon content. In contrast, NPG next the SSF variety finally, F- SSF

has lowest carbon content. Whereas carbon content decreases in the order of NPG > SSF > F-SSF.

The purity of the samples has been enhanced after acid digestion treatment. Because of most of their impurities were removed by the acid digestion treatment. Relatively three different varieties of graphite showed higher percentage of purity.

Table 01: Carbon content of the Raw and Purified graphite samples

Sample Name	Carbon Content (%)	
	Initial Purity (Raw Samples)	After Acid Digestion
NPG	98.90	99.99
F- SSF	97.46	99.00
SSF	97.50	99.50

(NPG- Needle Platy Graphite, SSF- Shiny Slippery Fibrous Graphite, F-SSF- SSF with very fine needles)

FTIR Analysis of Purified vein graphite

FTIR technique used widely to identify the formation of acidic group or an oxide layer on the graphite surface [9].

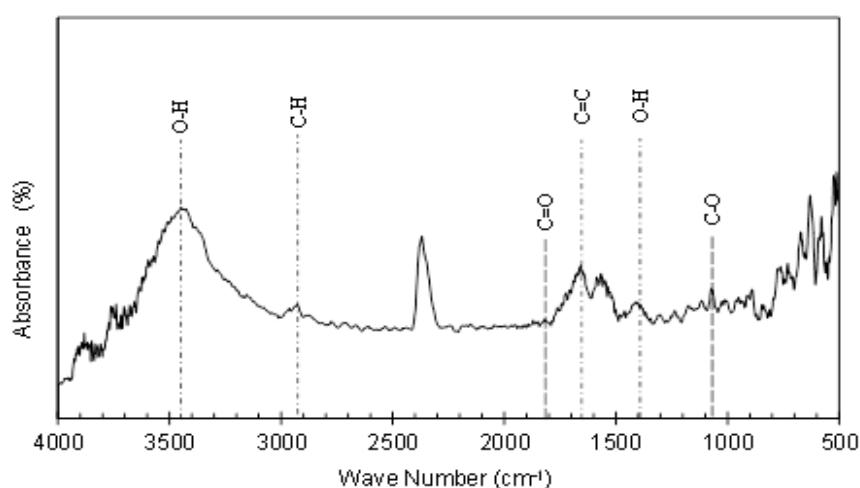


Figure 01: FTIR graphs of Purified NPG sample

Figure 01 shows the FTIR spectra of purified NPG variety. The applied acid digestion technique is able to conduct the surface modification simultaneously [9]. The broad band between 3500 and 3100 cm^{-1} attributed to the bending mode of the molecular water [13,14]. The vibrational bands of carbonyl group C=O stretching at 1720-1680 cm^{-1} , alkene group C=C stretching at 1637 cm^{-1} , O-H stretching at 1360 cm^{-1} and C-O stretching at 1160 cm^{-1} were introduced after the purification [9].

Figure 02 has the FTIR spectra for the purified NPG, modified with LiCl, NaCl and KCl respectively. In addition to the vibrational bond introduced by purification treatment, new peaks appeared for the relevant carbonate formation for each alkali chloride.

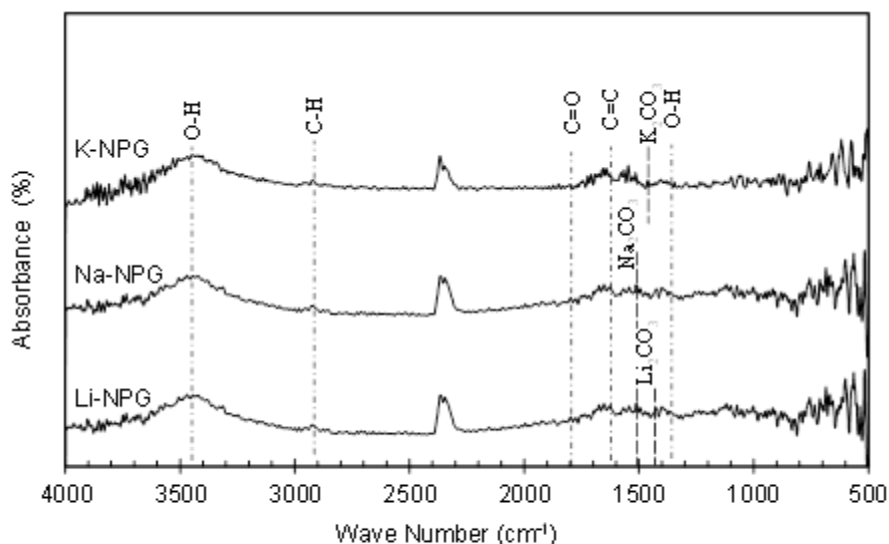


Figure 02: FTIR graphs of NPG sample treated with LiCl, NaCl and KCl

Figure 03 shows FTIR spectra of raw NPG variety. The broad band between 3500 and 3100 cm^{-1} attributed to the bending mode of the molecular water [13,14]. Further, minor peaks were due to incorporation of other impurities.

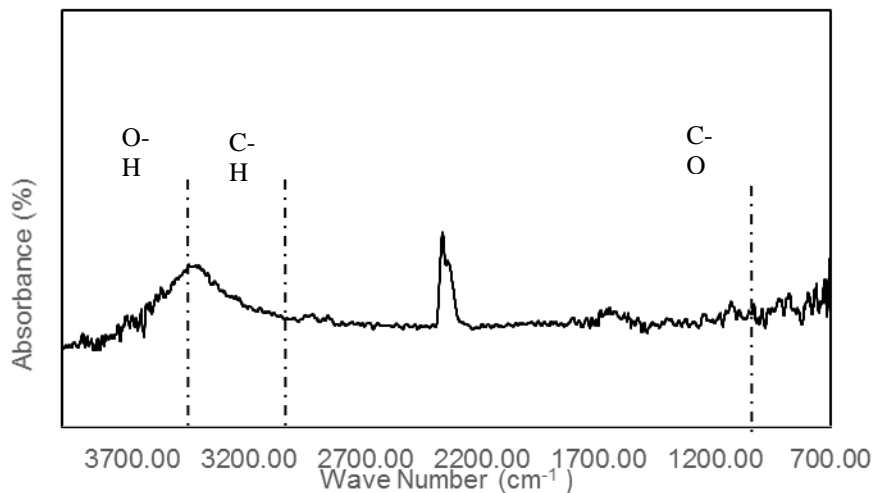


Figure 03: FTIR graph for raw NPG

Electrical Conductivity

D.C. electrical conductivity of three different raw graphite samples are indicated in table 02. The conductivity measurements were taken over the temperature range from 25 °C to 200 °C, at about 25 °C temperature interval during the cooling cycle. Both NPG and F-SSF varieties have a narrow conductivity variation, 3.0 -3.8 S cm⁻¹ and 3.1 -3.6 S cm⁻¹ respectively. However SSF shown 2.5 to 4.3 S cm⁻¹ variation with an increasing pattern with increasing temperature.

Table 02 – D.C conductivity variation with temperature, for the different morphologies of graphite in their raw form

Temp (°C)	Temp (K)	Conductivity (S cm ⁻¹)		
		NPG	F-SSF	SSF
200	473	3.0	3.4	4.3
150	423	3.8	3.4	4.3
100	373	3.7	3.3	4.1
75	348	3.6	3.2	4.0
50	323	3.5	3.1	3.7
25	298	3.3	3.6	2.5

Conductivity measurements were expressed according to Arrhenius equation (figure 03). The raw NPG behaves a straight line with positive gradient up to 150 °C and a sudden drop of the line was observed after 150 °C temperature. The raw F-SSF initially shows a negative gradient straight line within the temperature range of 25 °C to 50 °C and it after 50 °C it further continue as a straight line with different positive gradient was observed. The raw SSF shows a linear behavior with two different positive gradients.

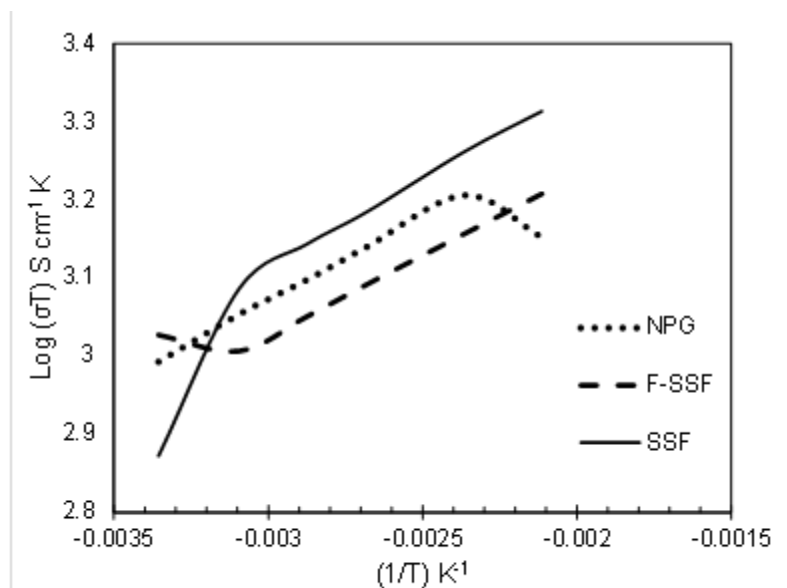


Figure 03 - Arrhenius plot of raw NPG, SSF and F-SSF morphological varieties

When $\log(\sigma T)$ is plotted against $(1/T)$, a straight line could be expected with the slope of $-(E/k)$ and an intercept on the $\log(\sigma T)$ axis of $\log A$. However, more and more analysis found that the $\log(\sigma T)$ vs $1/T$ plots show an unusual non-linear Arrhenius behavior, the absolute values of their slopes are high at low temperature and decrease gradually with increasing temperature. Such a phenomenon has been studied by some authors [12] and several particular functions have been proposed, based on assumption that the activation energy for conductivity is dependent on temperature.

For the purified samples, conductivity measurements were taken only at room temperature (25 °C). Low values of the conductivity were observed for the purified samples compared to the raw graphite (table 03). The electric conductivity is due to free movement of ions, and the impurity ions have been removed during the purification process. This is the major effect for the decrement of the conductivity. However, the π orbitals in graphite structure contain delocalized electrons across the hexagonal atomic sheets of carbon and contribute to graphite's conductivity after the purification.

The samples modified with LiCl, NaCl and KCl showed higher conductivity values than purified graphite (table 03). During the modification the alkali metal ions and chloride ions may have trapped within the graphite layers and measured conductivity value increased due to the additional free ions. Therefore applied alkali chloride coating were capable to improve the electric conductivity performance.

Table 03: Electrical Conductivity values of surface modified graphite samples

Sample Name	Conductivity, (S cm ⁻¹)				
	Raw	Purified	LiCl Treatment	NaCl Treatment	KCl Treatment
NPG	3.3	1.7	1.9	2.0	2.0
F- SSF	3.5	2.0	2.2	2.1	2.2
SSF	2.5	1.9	2.1	2.4	2.3

Modification of vein graphite with alkali chloride

Figure 4 shows the SEM analysis of the NPG treated with LiCl (A and B) and NPG morphological varieties (C and D). The microphotographs of C and D have shown closely packed thin plates of graphite, which is identical for the NPG morphology. The graphite sheets are formed by very fine fibrous material [4].

The needle like microstructure of graphite is formed by the growth of long, thin- bladed veins. The needle could be cleaved due to the fibrous nature of their arrangement. Long, fibrous needles of graphite were well crystallized, and short fibrous needle show an equigranular pattern which are evenly distributed and compacted [7]. The microphotographs of A and B have exhibited partly destroyed hexagonal sheets after surface modification.

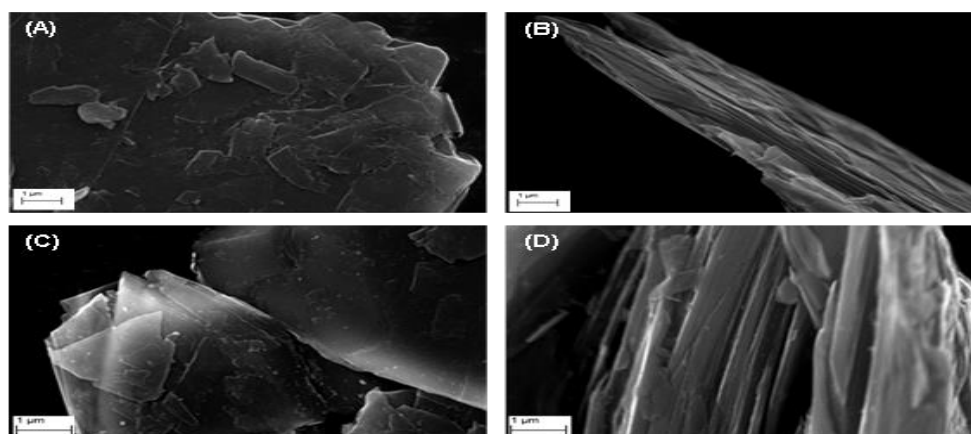


Figure 04 SEM images of the NPG treated with LiCl (A and B) and NPG morphological varieties taken from Ragedara Mine (C and D), performed with JSM 6400 and Gemini Zeiss ultra-scanning electron microscopes-back scattered and secondary electron mode.

CONCLUSION

The cost effective and convenient acid digestion method with a mixture of 5 % of HF, $\text{Con.H}_2\text{SO}_4$ & Con.HNO_3 have been studied and the vein graphite surface was modified using alkali chloride solutions for improving performance of a graphite electrode. The carbon content of the vein graphite has been enhanced after acid digestion treatment due to removal the impurities. The FTIR analysis proved that the new functional group bands have been introduced to the surface modified graphite. Higher conductivity of the treated graphite is due to free movement of ions, and the impurity ions have been removed during the acid digestion treatment and the modification with the alkali metal ions. All three varieties obey with linear Arrhenius behavior as well as raw NPG and F-SSF varieties were showed parabola, it may evidence for the semi conducting behavior.

ACKNOWLEDGEMENTS

The financial assistances from Innovative Research Grant-2013 of University Grant Commission of Sri Lanka and NRC Research Grant 15-007 are acknowledged.

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